

**Desorption Kinetics of H₂O, H₂, CO, and
CO₂ from Silica Reinforced Polysiloxane**

L.N. Dinh, M. Balooch

August 11, 1999

REC'D LIBRARY

◀ OCT 21 1999 ▶

REPORTS SECTION

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

VAULT REFERENCE COPY

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Work performed under the auspices of the U. S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

This report has been reproduced
directly from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (423) 576-8401
<http://apollo.osti.gov/bridge/>

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161
<http://www.ntis.gov/>

OR

Lawrence Livermore National Laboratory
Technical Information Department's Digital Library
<http://www.llnl.gov/tid/Library.html>

Desorption kinetics of H₂O, H₂, CO, and CO₂ from silica reinforced polysiloxane

L. N. Dinh, M. Balooch

Chemistry and Materials Science

Lawrence Livermore National Laboratory, Livermore, CA

ABSTRACT

We performed temperature programmed desorption up to 500K on silica-reinforced polysiloxane in both solid and foamed forms (M9787 and M9750 respectively). Our data show that H₂O was the dominant desorbing species in both forms of silicone (on the order of 100 μ g of physisorbed water and 900 μ g of chemisorbed water per gram of polymer), which are expected to be very hydrophilic when dehydrated. Detailed studies of the TPD spectra of H₂O from the silicones and from the fumed silica fillers suggest that H₂O molecules preferentially adsorbed on the surface of silica particles contained in the silicones with activation energies of desorption of 15 ± 3 kcal/mol and 50 ± 10 kcal/mol. There was strong evidence of H₂ desorption below 400K from the silicones. The equivalent concentration of H₂ in the silicones was 0.44 μ g of H₂ per gram of silicone. Other species desorbing from the silicones were CO, and CO₂ with concentrations on the order of 2.5 μ g, and 1.6 μ g per gram of silicone and activation energies of desorption of 10 ± 2 kcal/mol and 9.5 ± 1.5 kcal/mol, respectively.

I. INTRODUCTION

The M9787 silicone is composed of polysiloxane gumstock (67.6 weight %), fumed silica filler Cab-O-Sil M-7D (21.6 weight %), precipitated silica filler Hi-Sil 233 (4 weight %), and processing aid (6.8 weight %). The M9750 silicone used in our experiment has the same composition as that of the M9787, but with 50 % porosity. Silica occupies ~ 25 weight % in these silicones, and silica surfaces are well known to have a good affinity for water adsorption. Outgassing of water from these materials in a vacuum environment may be of some concern. In addition, the outgassing may change the nature of the silica/silicone bonding, even possibly the mechanical behavior of the materials. In an effort to understand the mechanism through which water is incorporated into the silicone structures and to effectively control the water content in them, we have carried out experiments on the adsorption and desorption of water on silicones, particularly M9787 and M9750. The outgassing of other detected gases like H₂, CO, and CO₂ from the silicones were also investigated.

II. EXPERIMENTS

380 μ m thick M9787 and 1.0 mm thick M9750 (50% porosity) silicone sheets were cut with a scissor into square samples with dimension of roughly 1cm x 1cm. These samples weighted roughly 0.048 ± 0.003 grams and 0.060 ± 0.005 grams for the M9787 and M9750 silicones, respectively. The square silicone samples were then coated on one

side with a few micrometer thick layer of ion-sputtered Au. Each sample was, next, enveloped in a Au foil with an opening of about 0.9 cm x 0.9 cm at one face such that the Au coated side of the sample was in contact with the Au foil (for a more uniform heat conduction over the entire back surface of the sample). In a typical experiment, the enveloped sample was held fixed, on the side, to a sample holder by ways of three mechanical clamps and transferred into an ultrahigh vacuum (UHV) chamber with a base pressure of 7.5×10^{-9} Torr (3×10^{-9} Torr in the detector chamber) through a differentially pumped load lock. A type K thermocouple was inserted in between the sample surface and a clamp holding the Au envelope for temperature measurement. The detector chamber is equipped with a quadrupole mass spectrometer (QMS). The QMS is computer controlled and can be multiplexed to monitor four mass-to-charge ratios simultaneously. Temperature Programmed Desorption (TPD) experiments were usually performed after the samples had been transferred into the UHV chamber for half an hour. During desorption experiments, the sample was positioned within 1 mm of the orifice (6 mm diameter) of the detector chamber. In this position, the axis of the QMS was along the sample normal and the sample surface was 22 cm from the ionization chamber. Particle desorption was thermally induced by a tungsten filament on the back side of the sample holder. The heating of the sample was computer controlled at a linear rate of 2 K/sec. The QMS was set up to detect positive ions and the signals produced by its electron multiplier were counted and stored in a computer.

In the water adsorption experiment, the sample was first dehydrated by thermal annealing at 500K until no water desorption could be found in subsequent TPD spectra (up to 500K) collected after the sample has returned to room temperature. Next, the sample

was exposed to water vapor at predetermined pressures for given amounts of time. The water coverages at given exposure conditions were, then, determined from the total amount of water desorbed from the corresponding TPD spectra in the 300K-500K window.

III. RESULTS & ANALYSIS

Fig. 1 shows typical TPD spectra of M9787 samples. From the spectra, it is clear that water was the dominant desorbing species for temperature up to 500K. Here, the integrated H₂O signal from 300 K-500 K is about 2 decades stronger than the combined signals from H₂, CO, and CO₂. The inset of fig. 1 shows the TPD spectra of H₂, CO, and CO₂ on a more sensitive scale. Since the desorbed signals grew stronger with increasing temperature instead of being flat over the desorption temperature range, we believe these desorbed molecules originated from within the M9787 samples.

The water desorption spectrum in fig. 1 could also be de-convolved into two spectra: I and II (fig. 2). The activation energies of desorption of water from each spectrum can be obtained from the following analysis.

The rate of desorption from unit surface can be written as:

$$-\frac{d\sigma}{dt} = \nu_n \sigma^n \exp(-E_d / RT) \quad (1)$$

where n is the order of the desorption reaction, σ is the surface coverage, ν_n is the rate constant, and E_d is the activation energy of desorption. All three kinetic parameters: n , ν_n , and E_d may be coverage dependent.

The differential approach involves the construction of an Arrhenius plot based on equation (1). This equation can be rearranged as:

$$\ln\left(-\frac{d\sigma}{dt}\right) = \ln(\nu_n \sigma^n) - \frac{E_d}{RT} \quad (2)$$

Or

$$\ln\left(-\frac{d\sigma/dt}{\sigma^n}\right) = \ln \nu_n - \frac{E_d}{RT} \quad (3)$$

The slope of the Arrhenius plot is:

$$\frac{d\left(\ln\left(-\frac{d\sigma/dt}{\sigma^n}\right)\right)}{d(1/T)} = \frac{-E_d(\sigma)}{R} + \frac{d\sigma}{d(1/T)} \left[\frac{\partial \ln \nu_n(\sigma)}{\partial \sigma} - \frac{1}{RT} \left(\frac{\partial E_d(\sigma)}{\partial \sigma} \right) \right] \quad (4)$$

When E_d and ν_n are coverage dependent, the interpretation of the Arrhenius plot is not simple! Fortunately, E_d and ν_n are, generally, independent of σ in systems with low coverage and without adsorbate-adsorbate interaction. In this case, equation (4) simplifies to equation (2), and the slope of the Arrhenius plot is $-E_d/R$. For a single TPD experiment (no knowledge on the dependence of E_d and ν_n on σ), equation (4) can still be reduced to equation (2) if the term $d\sigma/d(1/T)$ is negligible. This condition holds well at the onset of the desorption curve, during which coverage drops by no more than ten percent of its initial value.¹ Fig. 3 shows the Arrhenius plots for the two deconvolved TPD spectra I and II. The activation energies of water desorption obtained from the plot are 15 ± 3 kcal/mol and 50 ± 10 kcal/mol for spectra I and II respectively. Fig. 4 shows the TPD spectrum of water from fumed silica (Aerosil A-300) reported by Gun'ko's group.² The similarities between the TPD spectra of H_2O from M9787 and from fumed silica reported by Gun'ko et al. from 300K-500K suggest that H_2O molecules preferentially adsorbed on the surfaces of silica particles contained in M9787. The first

desorption peak in each spectrum is seen at about 425K- 435K. Desorbed water molecules that had been hydrogen bonded to one another and/or to OH groups were mostly responsible for this desorption peak ($n=1$).² The pre-exponential factor for this desorption process can be obtained from the intercept of the Arrhenius plot and are $4.3 \times 10^6 \text{ s}^{-1}$ and $8.1 \times 10^5 \text{ s}^{-1}$ for Gun'ko's group and our group, respectively. These values are much less than the typical solid lattice vibrational frequencies (10^8 - 10^{14} s^{-1}). This is another strong indication that these desorbed water molecules were not strongly bound to the surface of silica particles. Most of them were physisorbed on silica surfaces. For water molecules that had been formed by the breaking of Si-OH bonds and subsequently desorbed from the surface of silica particles ($n=2$), the pre-exponential factors are expected to be much closer to surface phonon frequencies.² Indeed, the pre-exponential factor for our deconvolved TPD spectrum II in fig. 2 was on the order of 10^7 - $5.2 \times 10^9 \text{ s}^{-1}$ and is also in agreement with those obtained by Gun'ko's group (10^7 - 10^{12} s^{-1}). An excellent illustration of water and hydroxyl reactions on silica surfaces has been published by Feng's group and is duplicated in this report as fig. 5.³ At $T > 673 \text{ K}$, even H_2O formation and desorption from isolated hydroxyl groups is possible according to this model. In Gun'ko's report, higher temperature formation and desorption of water from hydroxyl groups happens in the following upward order: desorption from dense island of OH groups, from vicinal or twin OH groups, and finally from isolated OH groups. The activation energies of desorption in Gun'ko's report are: 16 kcal/mol, 21-26 kcal/mol, 27-41 kcal/mol, and 42-60 kcal/mol for water that are hydrogen bonded to one another and/or to surface silanol groups, that are formed from dense islands of OH groups, that are formed from vicinal or twin OH groups, and that are formed from isolated OH groups

repectively. The activation energies for desorption of water from our experiments agree fairly well with those reported most recently from fumed silica and hydroxylated silica surface.²⁻⁴ There are published activation energies of desorption of water from silica surface that are in the range of 6-10 kcal/mol.^{5,6} The differences in the reported results have been explained in terms of effects of micropores, surface defects, and adsorbate interactions.^{4,7-10} It is interesting, however, to note that BET isothermal adsorption experiments have measured interaction energies of 12-18 kcal/mol for water on silanol surfaces, and that isosteric heat of adsorption measurements on quartz have also obtained adsorption energies of ~ 23 kcal/mol.¹¹

The activation energies of desorption for CO and CO₂ from M9787 were also measured to be $\sim 10 \pm 2$ kcal/mol and 9.5 ± 1.5 kcal/mol. These values are smaller than the activation energy of water desorption from M9787, so it is expected that CO and CO₂ in M9787 can be pumped away in a vacuum environment more easily than water. The pre-exponential factors for these desorption curves were in the range of 10^5 s^{-1} . Again, the low activation energies of desorption and pre-exponential factors from CO and CO₂ molecules suggest that they were of physisorbed. The CO/H₂O, CO₂/H₂O and CO/CO₂ ratios are plotted in fig. 6. There is no correlation between the water TPD spectrum and the CO or CO₂ TPD spectra. Unlike the case of CO and CO₂, the shape of the H₂ TPD spectrum qualitatively follows that of water TPD spectrum. The H₂⁺/H₂O⁺ ratio is almost constant at about 0.04 from 400 K-500 K (fig. 7). The H₂⁺/H₂O⁺ ratio obtained by cracking water molecules under similar vacuum condition was 0.025 ± 0.005 . The higher H₂⁺/H₂O⁺ ratio obtained from the M9787 sample may be explained by the additional breaking of 2 Si-OH bonds to form Si-O-O-Si + H₂ on the surface of silica, at

$T > 400\text{K}$. In any case, there was a strong correlation between the detected H_2^+ and H_2O^+ above 400K. The $\text{H}_2/\text{H}_2\text{O}$ ratio from 300K-400K was not flat, and actually had a peak at $\sim 350\text{K}$. This suggests an additional source of hydrogen with very low activation of energies of desorption from within the M9787 sample. This low activation energy desorption process have probably started below room temperature. Unfortunately, due to the non-exponential shape of the TPD spectrum from 300K-350K, the activation energy of desorption for this process cannot be measured.

There are 1.5×10^{17} water molecules desorbed (by integrating the desorption rate of the TPD spectrum in fig. 2 over the temperature range of 300-500 K) from a typical M9787 sample, which weights 0.048 grams. Following the above argument that water molecules desorb mainly from the surfaces of silica particles embedded in M9787, and taking the shape of the TPD spectrum reported by Gun'ko et al. as our model for water desorption beyond 500 K, the total number of water molecules that can be desorbed (or formed and then desorbed from OH groups) in 0.048 grams of M9787 is $\sim 1.5 \times 10^{18}$ molecules. The total weight percent of water in M9787 deduced from our data is, then, on the order of 0.1 (0.01 for physisorbed water and 0.09 for chemisorbed water). Note that the value of 0.01 weight percent for physisorbed water serves only as a lower limit, since the sample has been pumped down for many hours before TPD experiment. And it will be shown later on that physisorbed water can be effectively pumped out in a vacuum at room temperature. Our most recent microbalance experiment suggested that the weight percent of physisorbed water in M9787 can be on the order of 0.4.

Fig. 8 shows a plot of water coverage vs. exposure for a dehydrated M9787 sample. As mentioned previously, most water desorption and adsorption happen at the surfaces of

the silica particles scattered throughout the silicone matrix in M9787 samples.

Therefore, in this plot, the exposure and the coverage are not defined conventionally as the number of water molecules that strike or desorb per unit surface area of the M9787 silicone. The exposure, here, is defined as the number of water molecules that enter into a $380\text{ }\mu\text{m} \times 1\text{cm} \times 1\text{cm}$ box (containing suspended silica particles) with a square opening of $0.9\text{ cm} \times 0.9\text{ cm}$ during the water exposure period. To an approximation, we can think of the silicone matrix as almost transparent to water molecules. We first converted the water vapor pressure, at which the sample was exposed to, into the number of molecules striking a unit entrance surface area per second ($1 \times 10^{-6}\text{ Torr} \sim 3.78 \times 10^{14}\text{ molecules.cm}^{-2}.\text{sec}^{-1} \sim 1\text{ monolayer.cm}^{-2}.\text{sec}^{-1}$), then multiplied this number with the exposure time and the total entrance area of the box to get the total exposure (monolayers). The coverage is defined as the number of water molecules desorbed from the actual surfaces of the suspended silica particles out of the box in the temperature range from 300 K to 500 K. The coverage was obtained experimentally by first multiplying the number of water molecules striking a unit surface area of the orifice in the detector chamber per second by the total entrance area of the box, then integrating the signals over the time period spent to ramp the sample from 300K to 500K. The sticking coefficient of water on the silica surfaces in dehydrated silicone sample is defined as the slope of the plot of coverage vs. exposure. This sticking coefficient was ~ 0.2 at low exposure level, but dropped quickly at higher exposure. Note that the actual sticking coefficient over the whole desorption range of water from silica (up to 1000K) should be > 0.2 at sub-monolayer level of exposure. Dehydrated M9787 silicone and its derivatives are, thus, very hydrophilic.

Fig. 9 shows a typical TPD spectra of water from a M9787 sample (a), a similar M9787 sample which had been pumped in the ultrahigh vacuum chamber at a base pressure of 4×10^{-9} Torr (9×10^{-10} Torr in the detector chamber) for 3 days (b), and a M9750 sample (foam) with similar weight which had been pumped down in a similar UHV environment for 5 days (c). Due to experimental difficulties, the actual desorption range for curves [b] and [c] were only from 360K-500K.¹² Our experimental results verified that the water desorption rate in M9750 was not higher than that of M9787 with similar weight, given that the total surface area of a typical M9750 sample in our experiments was 4 times larger than that of a M9787 sample with similar weight. This observation is in consistent with a model involving water molecules desorbing from the surfaces of silica particles in M97xx silica-reinforced polysiloxane. It is also noted that the total number of water molecules desorbed (TPD up to 500K) from two similar M9787 samples can be different by more than a factor of 2, depending on how long the samples were pumped down in the ultrahigh vacuum chamber prior to TPD experiment. This observation suggests that physically adsorbed water molecules in M9787 can be effectively pumped out in a vacuum chamber at room temperature. In fact, if we replace $-E_d/R$ and $v_n \sigma^n$ in equation (2) with the slope and the intercept of the Arrhenius plot for the deconvolved desorption spectrum I in fig. 2, it would be possible to predict how fast the physisorbed and the chemisorbed water molecules can be pumped out of the M9787 based silicones in a good vacuum (assuming no readsorption of water molecules on silica surfaces). In fig. 10, we computed the weight percent of physisorbed water retained per gram of M9787 as a function of pumping time. From the plots, it is seen that most physisorbed water can be pumped out at room temperature in a reasonable amount

of time (60 hours). However, due to higher activation of energies of desorption, most chemisorbed water will retain in the sample after 100 years of pumping time at room temperature.

IV. CONCLUSION

TPD experiments show that H_2O desorbed from the surfaces of silica particles contained in the silicones with two different activation energies of desorption of 15 ± 3 kcal/mol and 50 ± 10 kcal/mol. The sticking coefficient of water molecules on the dehydrated surfaces of silica particles in the silicones were higher than 0.2 at sub-monolayer exposure. The other desorbing species are H_2 (below 400K), CO, and CO_2 . The activation energies of desorption of CO and CO_2 were measured to be 10 ± 2 kcal/mol and 9.5 ± 1.5 kcal/mol. The weight percentages of chemisorbed water, H_2 , CO, and CO_2 inferred from our TPD experiments were on the order of 0.09, 0.00043, 0.00017, and 0.000072. The weight percentage of physisorbed H_2O can be on the order of 0.4. Based on the measured data, we have also shown that it is possible to pump out most of the physisorbed water at room temperature in a reasonable time scale, while most of the chemisorbed water would remain intact on the surface of the silica fillers even up to 100 years, if kept at room temperature.

V. ACKNOWLEDGEMENT

We would like to thank Dr. J. D. Lemay for support and useful discussion. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

REFERENCES

1. J. B. Miller et al., *Journal of Chemical Physics* **87**, 6725 (1987).
2. V. M. Gun'ko et al., *Journal of Mass Spectrometry and Ion Processes* **172**, 161 (1998).
3. A. Feng et al., *Journal of Colloid and Interface Science* **180**, 276 (1996).
4. O. Sneh et al., S. M. George, *Surface Science* **364**, 61 (1996).
5. G. M. Nishioka et al., *Journal of Colloid and Interface Science* **105**, 102 (1985).
6. L. T. Zhuralev, *Colloids Surfaces A* **74**, 71 (1993).
7. K. Klier et al., *Journal of Physical Chemistry* **77**, 1458 (1973).
8. J. H. Shen et al., *Colloid Interface Science* **75**, 56 (1980).
9. Z. El Rassi et al., *Journal of Chromatography* **125**, 179 (1976).
10. W. A. Patrick et al., *Journal of Physical Chemistry* **29**, 1031 (1925).
11. J. W. Whalen, *Journal of Physical Chemistry* **65**, 1676 (1961).
12. The W filament used in heating the sample was shorted out during our first attempt to do TPD on this sample at 360 K. The experiment was stopped for 10 minutes, while

we tried to reverse the problem. Since we have desorbed water up to 360 K, the TPD spectrum presented here only went from 360 K-500K.

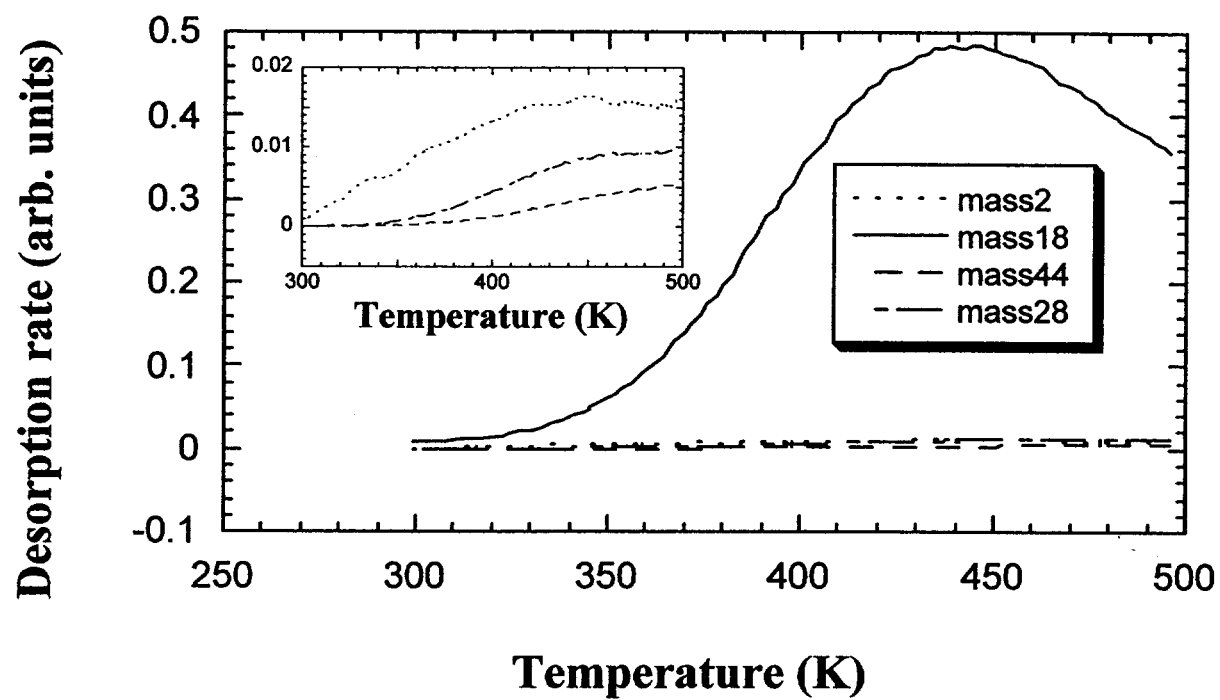


Fig. 1: A typical TPD spectrum from M9787 samples.

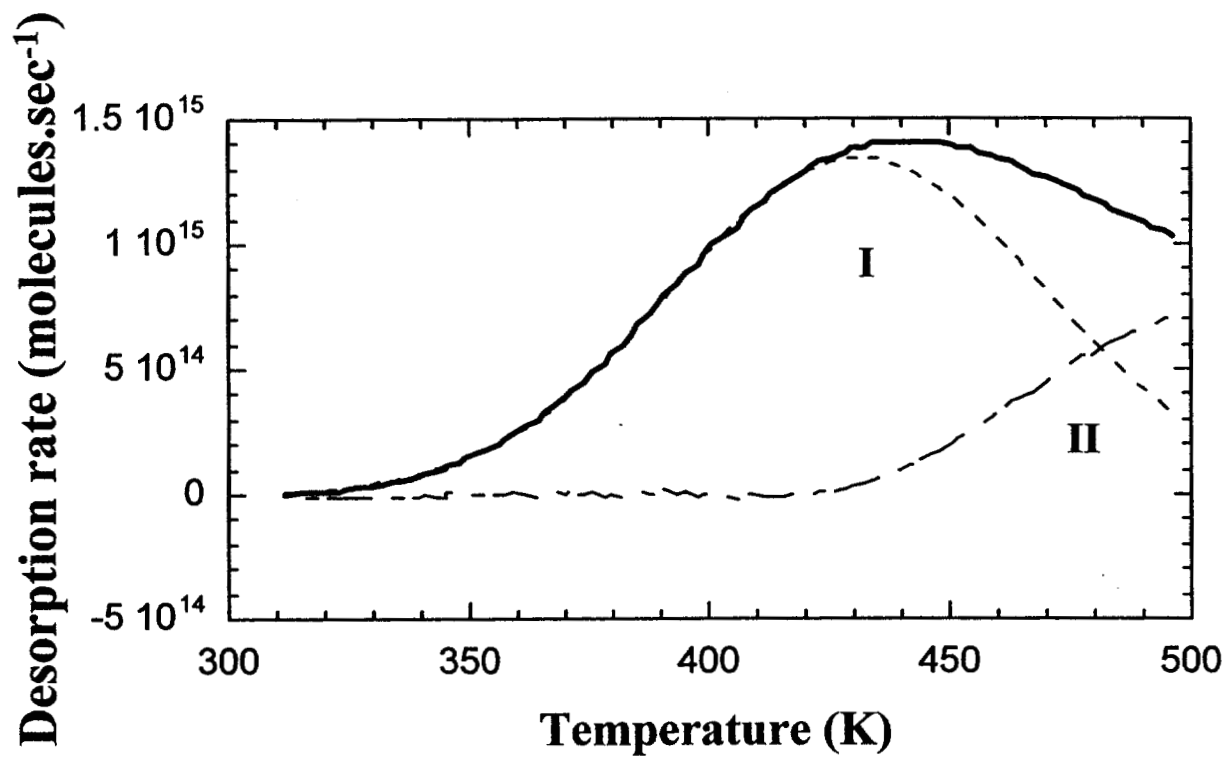


Fig. 2: A typical H₂O TPD spectrum from M9787 can be de-convoluted into two spectra: I and II.

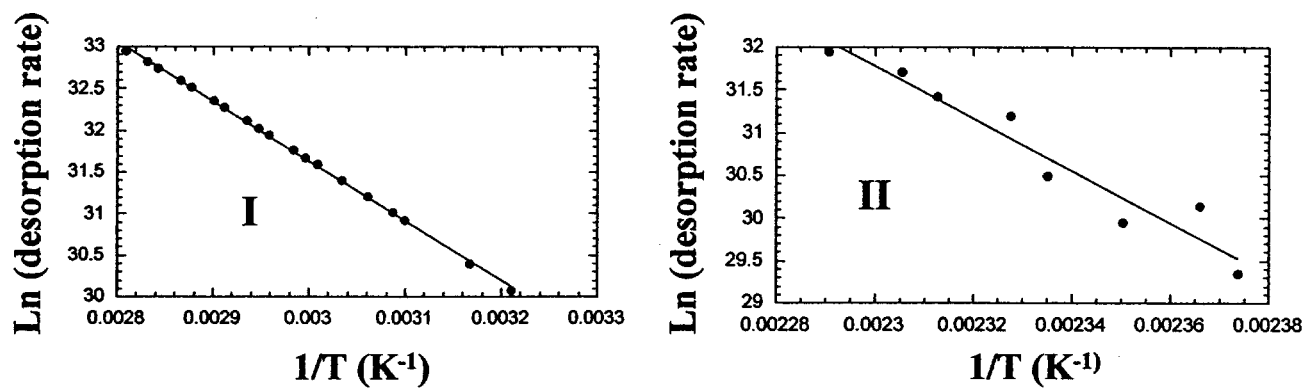


Fig. 3: The Arrhenius plots for the two deconvolved TPD spectra: I and II

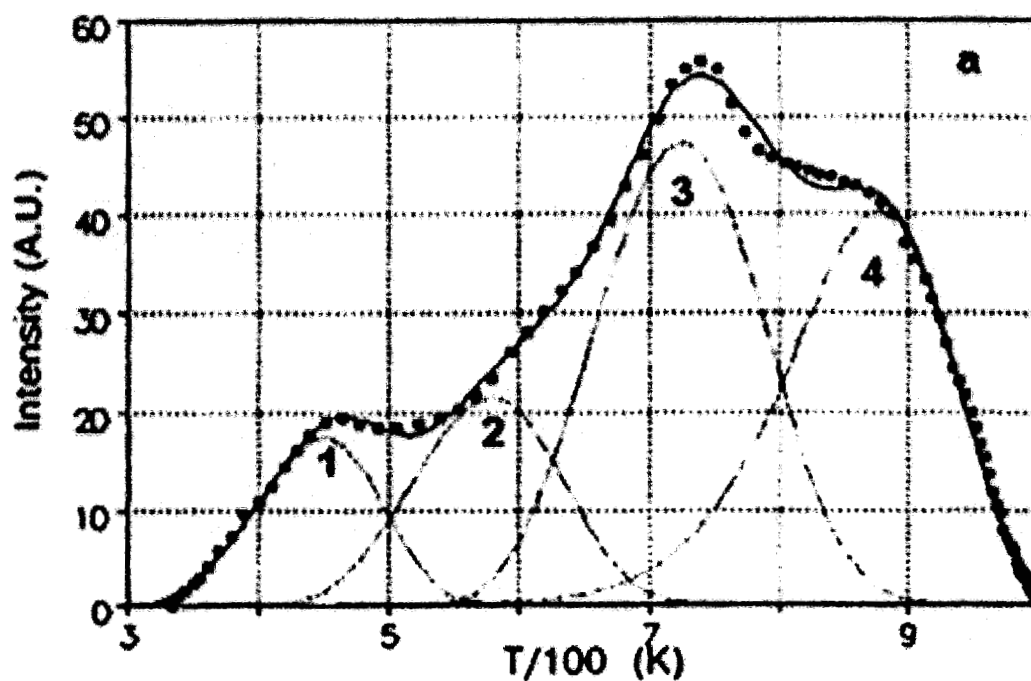


Fig. 4: A typical TPD spectrum of H_2O from fumed silica reported by Gun'ko's group.² The activation energies of desorption of water are: $E_1 \sim 16$ KCal/mol, $E_2 \sim 21 - 26$ KCal/mol, $E_3 \sim 27 - 41$ KCal/mol, $E_4 \sim 42 - 60$ KCal/mol

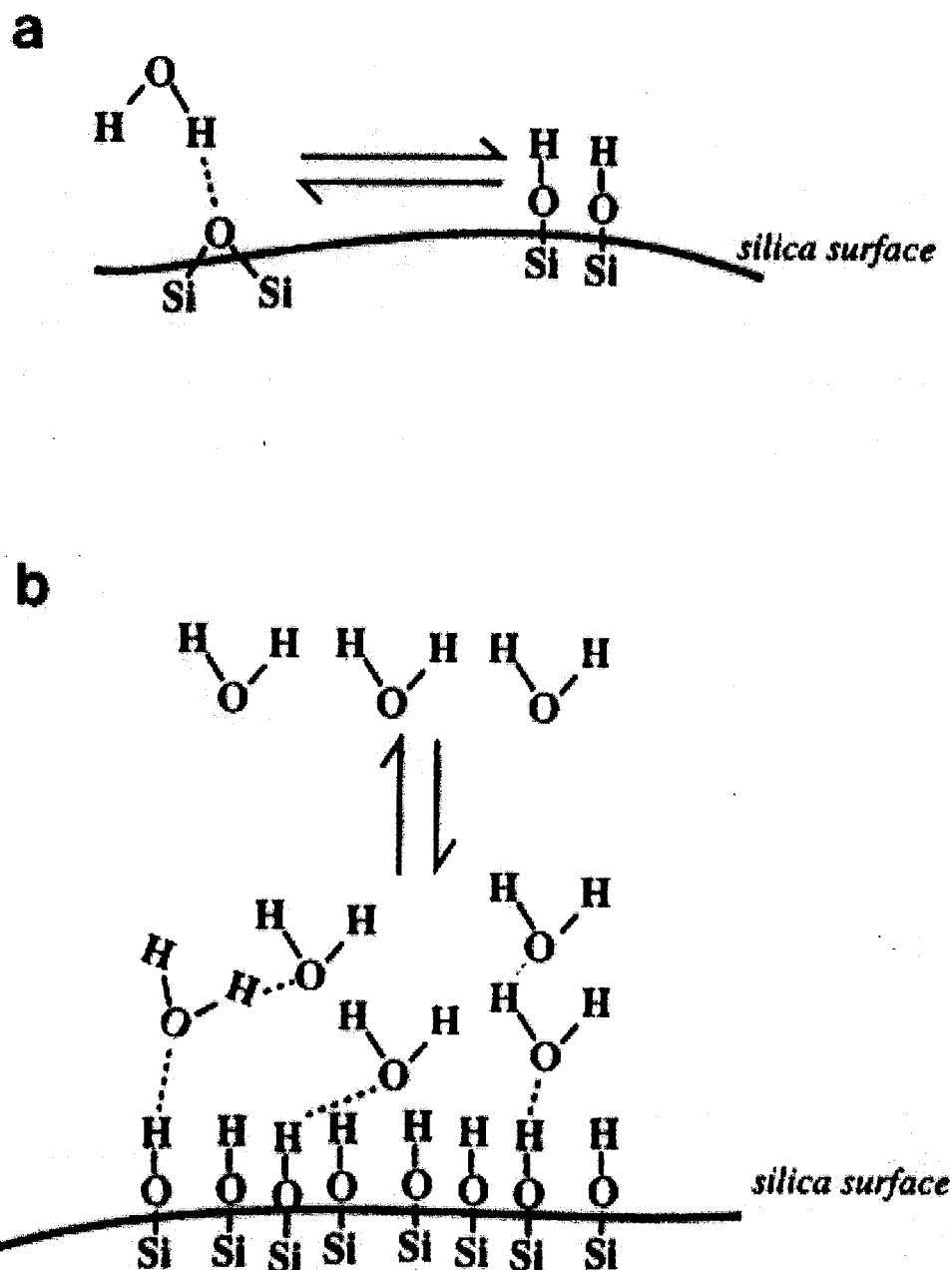


Fig. 5: Illustration of water and hydroxyl reactions on silica surfaces for two temperature regions (by Feng's group⁴): (a) at $T > 400\text{ }^{\circ}\text{C}$, dehydroxylation and rehydroxylation; (b) at $T < 400\text{ }^{\circ}\text{C}$, adsorption and desorption of H_2O on hydroxyl group.

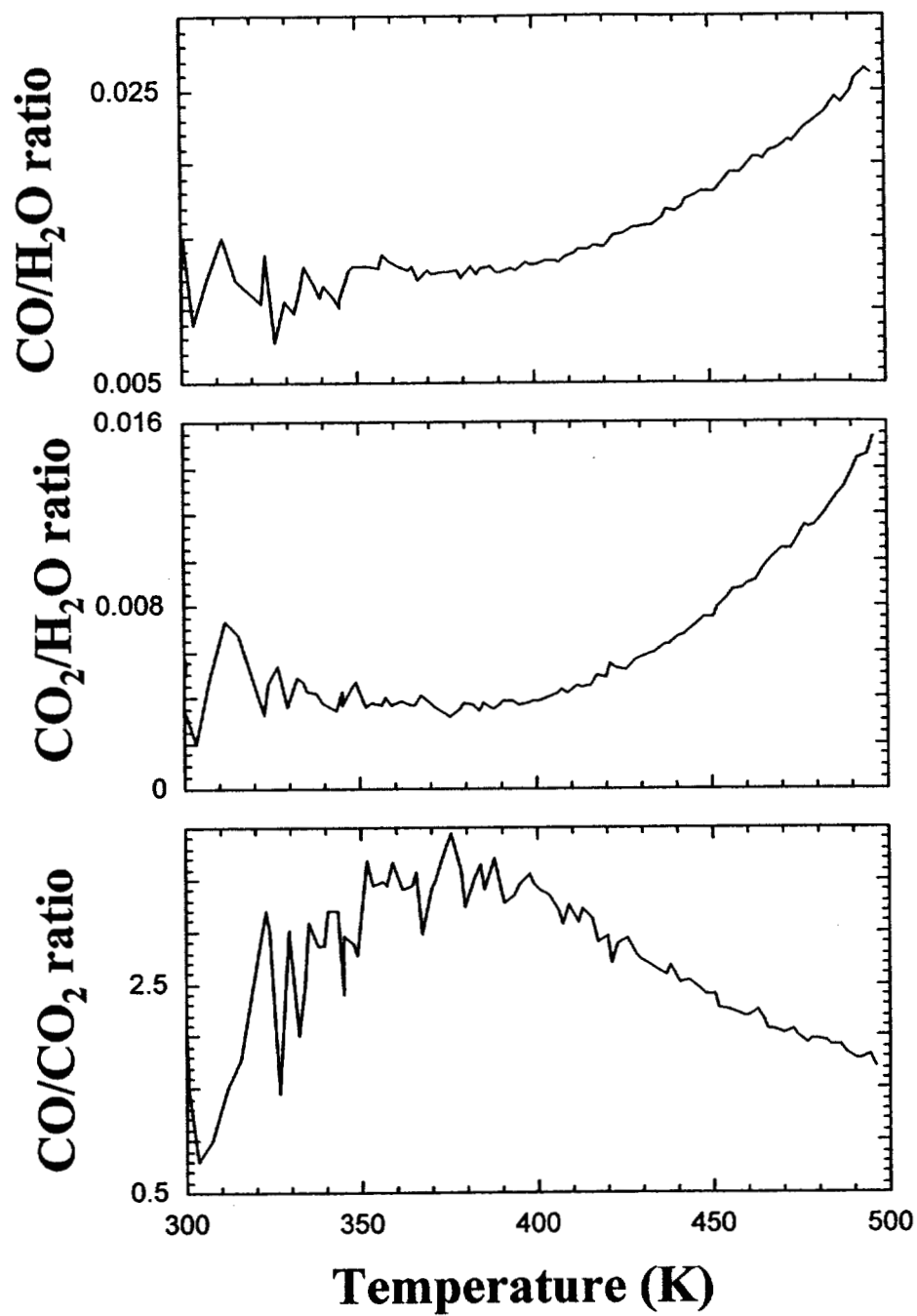


Fig. 6: The CO/H₂O, CO₂/H₂O and CO/CO₂ ratios.

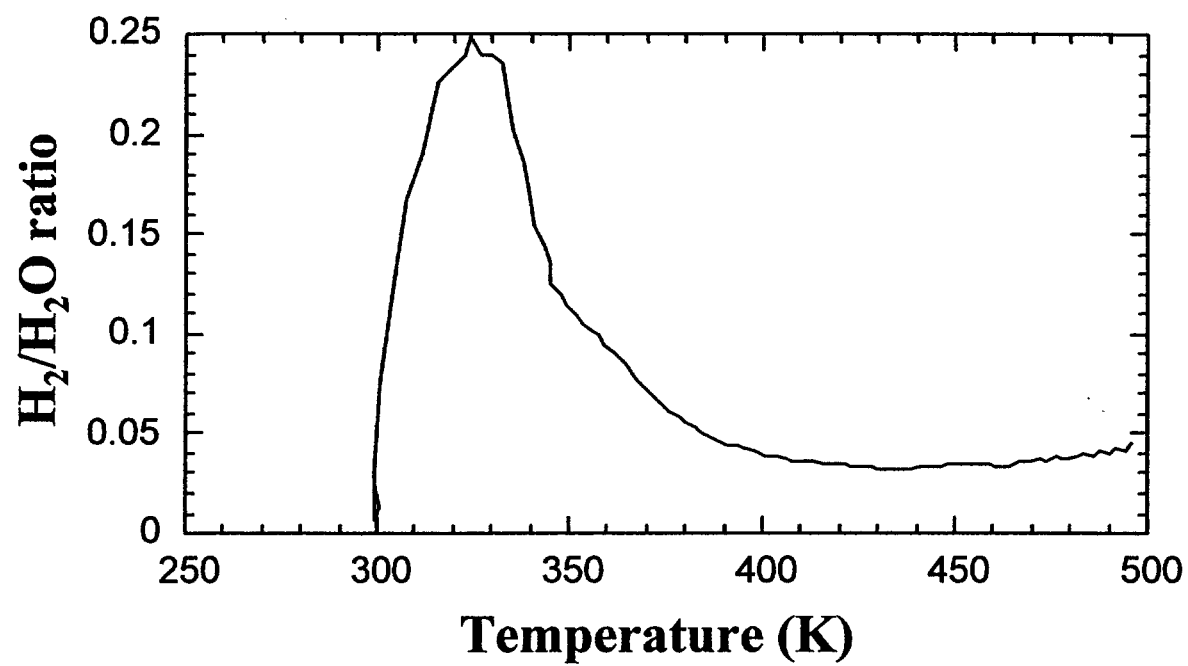


Fig. 7: the $\text{H}_2/\text{H}_2\text{O}$ ratio

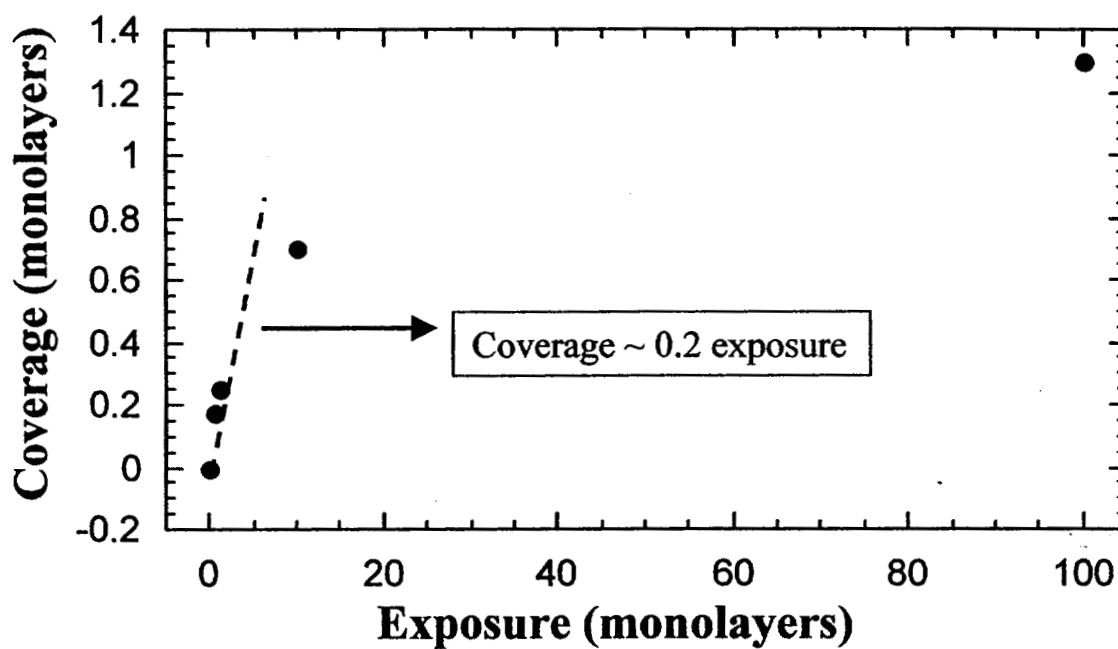


Fig. 8: A plot of water coverage vs. exposure for a dehydrated M9787 sample.

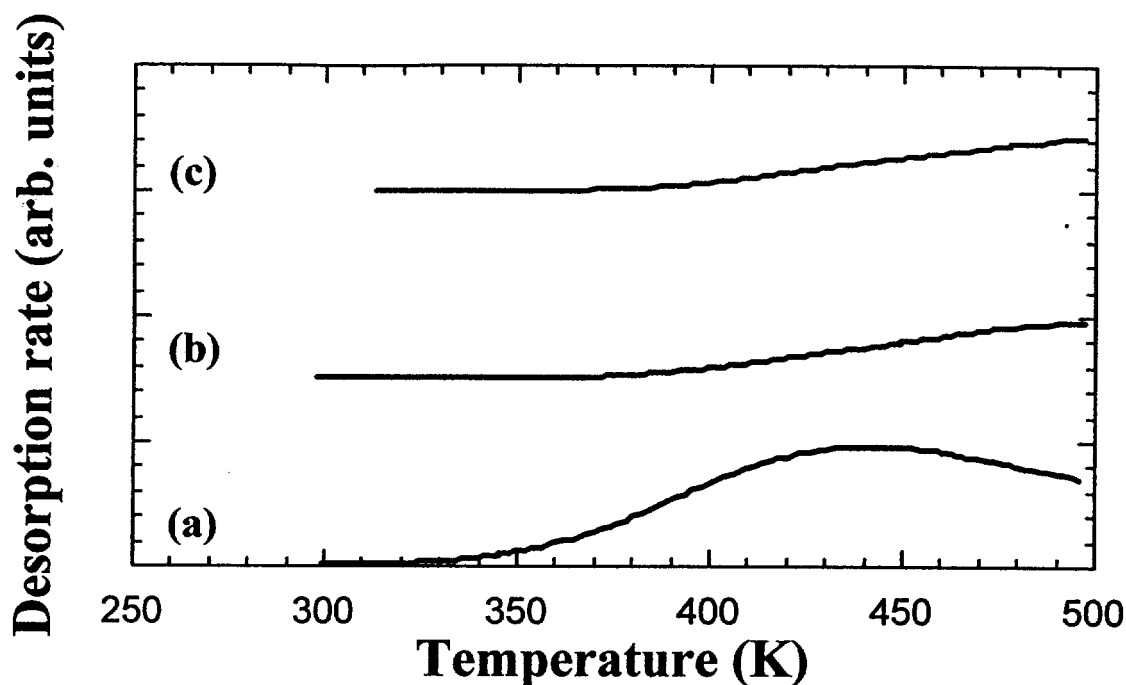


Fig. 9: TPD spectra of water from a typical M9787 sample [a], from another M9787 sample which had been pumped in the ultrahigh vacuum chamber at a base pressure of 4×10^{-9} Torr (9×10^{-10} Torr in the detector chamber) for 3 days [b], and from a M9750 sample (c) which had been pumped down in an UHV environment similar to the M9787 sample in curve [b] for 5 days. The spectra are shifted vertically for easy display.

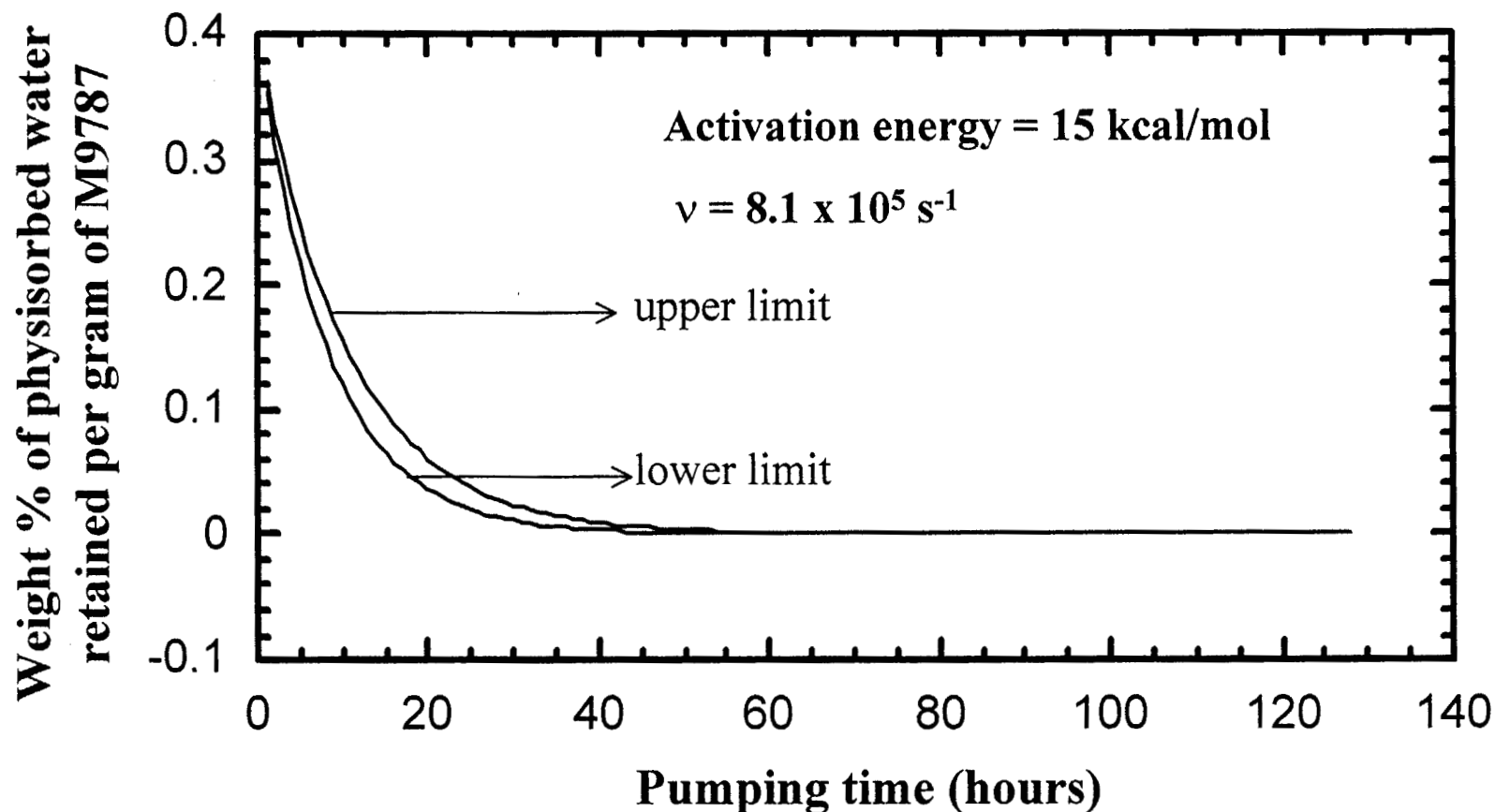


Fig. 10: It is possible to pump out all the physisorbed water at room temperature in a reasonable amount of time (< 60 hours) if the weight percentage of physisorbed water per gram of M9787 silica-reinforced polysiloxane is on the order of 0.4

